

Charge order and the metal-insulator transitions in $A_{1/2}A'_{1/2}\text{MnO}_3$

Michel van Veenendaal* and A. J. Fedro

Northern Illinois University, De Kalb, Illinois 60115

and Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

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An interpretation is given for the metal-insulator transitions occurring in $A_{1/2}A'_{1/2}\text{MnO}_3$ using the double-exchange model but including the coupling of the electron to the Jahn-Teller distortions and a finite Coulomb interaction between electrons in the twofold degenerate e_g orbitals. We find that, whereas the ferromagnetic state is metallic, the insulating state is polaronic. As one lowers the temperature, a transition from the ferromagnetic state to the *CE* phase is observed, which is, due to the strong phonon renormalization of the bandwidth, accompanied by a change in resistivity of several orders of magnitude. In order to obtain the observed magnetic structure, i.e., *CE* type, it is essential to include the lowering of the on-site energy due to polaronic self-energy effects. We present a way of building the charge-ordered magnetic structures out of small units of a “localized” $3z^2-r^2$ polaron with four antiferromagnetic and two ferromagnetic neighboring t_{2g} core spins. [S0163-1829(99)00923-6]

The unusual magnetic and electronic properties of the perovskites $A_{1-x}A'_x\text{MnO}_3$, where A and A' are trivalent and divalent cations respectively, have attracted considerable attention. In these systems the Mn-O-Mn bond angle can be changed by using cations of different radii. This causes a change in the ratio of the effective hopping to the t_{2g} superexchange. In carefully tuned samples one has been able to induce a metal-insulator transition as a function of, e.g., temperature, magnetic field,^{1,2} applied current,³ or by irradiation with visible light⁴ or x rays.⁵ These transitions are different from the usual colossal magneto-resistance effect in that they are accompanied by changes in crystal, electronic, and magnetic structure. The insulating system is observed to be the *CE*-type structure.⁶ This structure (shown in Fig. 3) is charge ordered and has ferromagnetic chains that zigzag in the xy plane. An explanation of this *CE* phase is crucial to the understanding of the metal-insulator transitions.

A number of explanations have been given for the *CE*-type structure. Interpretations based on static lattice distortions^{7,8} can show some charge order, but are unable to explain the large jump in resistivity. Charge order can also be a result of a strong near-neighbor Coulomb interaction. For an unrenormalized effective bandwidth of $\sim 0.2\text{--}0.3$ eV, large Coulomb interactions of the order of 1.6–2.4 eV are necessary.⁹ A strong renormalization of the bandwidth by, e.g., polaronic effects,¹⁰ could severely lower the required near-neighbor Coulomb interaction. However, it would also strongly reduce the double-exchange interaction.^{11–13} This would imply that, unless the t_{2g} superexchange is also renormalized, the spins would prefer the pure antiferromagnetic alignment, i.e., the *G*-type structure.⁶ A reduction of the superexchange is unlikely, since the t_{2g}^3 state is not strongly modified by polaronic effects. Furthermore, no significant change in critical temperatures is observed when going from the ferromagnetic to the *CE*-type structure, indicating that the coupling constants are of the same order of magnitude in both phases. Another argument against the presence of a strong near-neighbor Coulomb interaction is that the charge

order in the xy plane reproduces itself along the z axis. This means that a (formally) Mn^{3+} ion is surrounded by four Mn^{4+} and two Mn^{3+} ions, which is not what one would expect for this Coulomb interaction.

We show here that the transition from the ferromagnetic to the *CE* phase is a transition from a nonpolaronic to a polaronic regime. In the polaronic state the mobility of the effective quasiparticles is strongly reduced. However, in the *CE* structure, ferromagnetic bonds are present as a result of the double-exchange mechanism, indicating that the kinetic energy of the e_g electrons is still sufficient to overcome the superexchange energy of the t_{2g} spins. We show here that this apparent contradiction can be explained from the fact that the conduction properties are a result of the coherent motion of the quasi particles (given by taking the expectation value of the phonon operators including only diagonal transitions yielding a first order effect, i.e., $t_{\text{eff}} \cong te^{-\gamma^2 g}$), whereas the ferromagnetic alignment of neighboring core spins is a consequence of the lowering of the on-site polaronic self-energy ε_p due to the inclusion of virtual second order processes (i.e., the effect of nondiagonal transitions) which are of the order t^2 . For simplicity, we consider here the situation for $x=0.5$.

We assume here that the spins of the itinerant e_g electrons are parallel to the t_{2g} core spins as a result of the strong Hund's coupling. This leads to effectively spinless e_g electrons with an orbital degeneracy $\alpha = 1, -1 = x^2 - y^2, 3z^2 - r^2$. The Hamiltonian for the e_g electrons and the phonons is given by

$$H = \sum_{i\alpha, j\alpha'} t_{i\alpha, j\alpha'} \left\langle \cos \frac{\theta_{ij}}{2} \right\rangle c_{i\alpha}^\dagger c_{j\alpha'} + U \sum_i n_{i1} n_{i,-1} + \hbar \omega \sum_i b_i^\dagger b_i + \sqrt{\varepsilon_p \hbar \omega} \sum_{i\alpha} (b_i^\dagger + b_i) \alpha n_{i\alpha}, \quad (1)$$

where $c_{i\alpha}^\dagger$ creates an e_g electron on site i with orbital index α and b_i^\dagger a quantized Jahn-Teller distortion. The first term describes the hopping and the second the on-site Coulomb in-

interaction with strength U . The transfer matrix elements t follow the usual Slater-Koster relationships¹⁴ for d electrons. The factor $\langle \cos(\theta_{ij}/2) \rangle$ describes the double-exchange effect on the hopping-matrix element in the classical limit,¹² where θ_{ij} is the angle between the core spins on sites i and j and $\langle \dots \rangle$ denotes the thermal average. The third term describes the quantized Jahn-Teller distortions with phonon energy $\hbar\omega$. The last term gives the coupling of the electrons to the Jahn-Teller distortions with ε_p the polaron energy. The core spins interact with each other via a near neighbor superexchange term

$$H_{\text{sup}} = J \sum_{\langle ij \rangle} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = JS^2 \sum_{\langle ij \rangle} \langle \cos \theta_{ij} \rangle. \quad (2)$$

The Jahn-Teller distortions are treated using the variational Lang-Firsov approach,^{15,16} which employs a canonical transformation $\bar{H} = e^S H e^{-S}$ where $S = -\gamma \sqrt{g} \sum_{i\alpha} (b_i^\dagger - b_i) \alpha n_{i\alpha}$, where $g = \varepsilon_p / \hbar\omega$ and γ the degree of the polaronic effect. The Coulomb interaction is treated by the introduction of auxiliary boson operators¹⁷ e_i , $p_{i\alpha}$, and d_i , that give the occupation number of the empty, singly occupied with orbital index α , and doubly occupied electron states at site i , respectively. The Hamiltonian now transforms into $\bar{H} = V + H_{\text{polaron}}$. H_{polaron} is given by

$$H_{\text{polaron}} = U \sum_i d_i^\dagger d_i - \varepsilon_p (2 - \gamma) \gamma \sum_{i\alpha} (n_{i\alpha} - d_i^\dagger d_i). \quad (3)$$

We have neglected the usual residual term in \bar{H} whose expectation is zero when one considers diagonal transitions, i.e., involving no change in the number of phonons.

The effective quasiparticle Hamiltonian is now given by

$$V = \sum_{i\alpha, j\alpha'} \bar{t}_{i\alpha, j\alpha'} \xi_{i\alpha, j\alpha'}(0) \bar{c}_{i\alpha}^\dagger \bar{c}_{j\alpha'} \quad (4)$$

with

$$\bar{t}_{i\alpha, j\alpha'} = t_{i\alpha, j\alpha'} \left\langle \cos \frac{\theta_{ij}}{2} \right\rangle z_{i\alpha} z_{j\alpha'}, \quad (5)$$

where we have used the Kotliar-Ruckenstein formalism¹⁷ for the operators $z_{i\alpha}$,

$$z_{i\alpha} = (1 - p_{i\alpha}^\dagger p_{i\alpha} - d_i^\dagger d_i)^{-1/2} (e_i^\dagger p_{i\alpha} + p_{i, -\alpha}^\dagger d_i) \times (1 - p_{i, -\alpha}^\dagger p_{i, -\alpha} - e_i^\dagger e_i)^{-1/2}. \quad (6)$$

We adopt the saddle-point approximation, where the boson operators are considered to be independent of space and time. The phonon operators are given by

$$\xi_{i\alpha, j\alpha'}(t) = e^{-\gamma \sqrt{g} [\alpha (e^{i\omega t} b_i^\dagger - e^{-i\omega t} b_i) - \alpha' (e^{i\omega t} b_j^\dagger - e^{-i\omega t} b_j)]}, \quad (7)$$

where the time-development will be needed later on. The expectation value of the phonon operator for diagonal transitions leads to a renormalization of the hopping matrix element by $\langle \xi_{i\alpha, j\alpha'}(t) \rangle = \exp(-\gamma^2 g)$. In the polaronic limit, $\gamma = 1$, this gives the well-known result that the polaronic bandwidth is given by $4tDe^{-g}$ with D the dimension.¹⁸ Millis¹⁹ gives an estimate of g of 6–20 indicating a reduction of the

effective bandwidth by more than two orders of magnitude. Exact diagonalizations show that this is indeed a good approximation for the quasiparticle bandwidth.²⁰ However, they also show that the ground-state energy is not well described by the Lang-Firsov approximation for comparable energy scales, i.e., $\varepsilon_p \sim t$. This is due to the neglect of processes where the virtual creation and annihilation of phonons is involved. We describe here these contributions to the ground-state energy to order t^2 . The electron dynamics are given by the Green's function $G_{i\alpha, j\alpha'}(z) = -(i/\hbar) \int_0^\infty dt e^{(i/\hbar)(E+i\eta)t} \langle \bar{c}_{i\alpha}(t) \bar{c}_{j\alpha'}^\dagger(0) \rangle \equiv -(i/\hbar) \int_0^\infty dt e^{(i/\hbar)zt} \langle \bar{c}_{i\alpha} e^{-(i/\hbar)Vt} \bar{c}_{j\alpha'}^\dagger \rangle$ with $z = E + \varepsilon_p(2 - \gamma) + i\eta$. This Green's function is given by

$$G_{i\alpha, j\alpha'}(z) = G^0(z) \left[\delta_{i\alpha, j\alpha'} + \sum_{j''\alpha''} [\bar{t}_{i\alpha, j''\alpha''} \langle \xi_{i\alpha, j''\alpha''}(0) \rangle + M_{i\alpha, j''\alpha''}(z)] G_{j''\alpha'', j\alpha'}(z) \right], \quad (8)$$

where $G^0(z) = 1/z$. The memory function gives the contributions due to incoherent hopping processes, i.e., involving exchanges of one or more phonons

$$M_{i\alpha, j\alpha'}(z) = \sum_{j\tilde{\alpha}} \bar{t}_{i\alpha, j\tilde{\alpha}} \bar{t}_{j\tilde{\alpha}, j\alpha'} \langle 1 - n_{j\tilde{\alpha}} \rangle X_{i\alpha, j\tilde{\alpha}}^{\tilde{\alpha}, j\alpha'}(z). \quad (9)$$

The effect of coupling to the Jahn-Teller distortions is obtained by evaluating the phonon averages

$$\begin{aligned} X_{i\alpha, j\tilde{\alpha}}^{\tilde{\alpha}, j\alpha'}(z) &= \int_0^\infty dt e^{i(z/\hbar)t} \\ &\times \left(-\frac{i}{\hbar} \langle \xi_{i\alpha, j\tilde{\alpha}}(t) \xi_{j\tilde{\alpha}, j\alpha'}(0) \rangle - e^{-2\gamma^2 g} \right) \\ &= e^{-2\gamma^2 g} \int_0^\infty dt e^{i(z/\hbar)t} \\ &\times \left(-\frac{i}{\hbar} e^{\gamma^2 g(1 + \alpha\alpha' \delta_{i,j}) e^{-i\omega t}} - 1 \right) \\ &= e^{-2\gamma^2 g} \sum_{n=1}^\infty \frac{1}{n!} [\gamma^2 g(1 + \alpha\alpha' \delta_{i,j})]^n \frac{1}{z - n\hbar\omega}. \end{aligned} \quad (10)$$

Different processes contribute to the memory (i.e., self-energy) function. For $i \neq j$ one generates the incoherent next-nearest-neighbor hopping terms and for $i = j$ one obtains the on-site lowering of the polaronic binding energy. Numerically, we find that the latter effect is large as compared to the incoherent hopping which is essentially proportional to the coherent hopping squared [i.e., $t_{\text{incoh}} = (te^{-\gamma^2 g})^2$] and thus very small. Note also, that the self-energy term is zero for $\alpha \neq \alpha'$.

In the manganites the appearance of different magnetic structures can be described as a competition between ferromagnetic regions of different dimension and the number of antiferromagnetic bonds.²¹ For the F , A , C , and G type structures the ferromagnetic region has dimension 3, 2, 1, and 0,

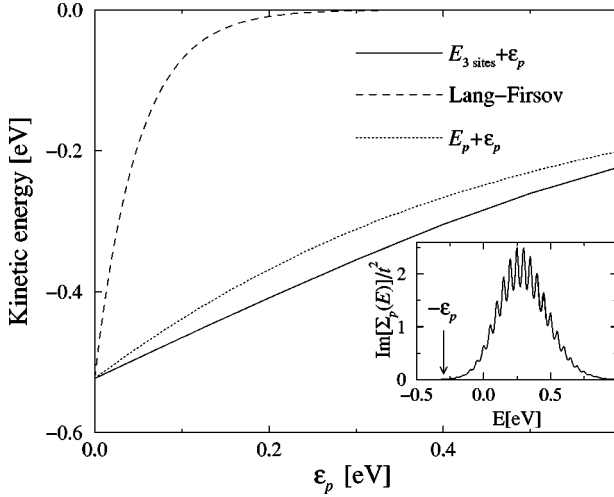


FIG. 1. Calculations of the effective kinetic energy for a three-site cluster by exact diagonalization, $E_{3 \text{ sites}} + \varepsilon_p$ (solid line), and by evaluation of the Green's function in Eq. (8) with (dotted line, $E_p + \varepsilon_p$) and without (dashed line, Lang-Firsov approximation) the memory function $M_{i\alpha,j''\alpha''}(z)$. We have used $t=0.37$ eV and $\hbar\omega=50$ meV. The inset shows the imaginary part of the self-energy for $\varepsilon_p=0.3$ eV. For clarity a broadening of $\eta=0.04$ eV has been used.

respectively, whereas the number of antiferromagnetic bonds increases from 0, 2, 4, to 6 per site, respectively. The *CE* structure is similar to the *C* structure, except that the ferromagnetic chains are not linear, but zigzag in the *xy* plane. In *C*-type structures an electron can hop, at low temperatures, to two of the six neighboring sites due to the $\langle \cos(\theta_{ij}/2) \rangle$ factor. The effect of the self-energy on the effective kinetic energy is directly seen by studying the coupling of a polaron with two neighboring empty sites. In the Lang-Firsov approximation ($M_{i\alpha,j''\alpha''} \rightarrow 0$) the nearest-neighbor spins have to be aligned by coherent hopping of the polaron. The kinetic energy, i.e., the double-exchange energy, is then given by $\sqrt{2}t \exp(-\varepsilon_p/\hbar\omega)$, see Fig. 1. This energy is certainly less than the superexchange energy JS^2 for $\varepsilon_p > 0.2$. Thus, in this approximation, the completely antiferromagnetic state, denoted as the *G* type,⁶ is found to be more favorable. However, comparison with the results of an exact diagonalization of *H* for three sites, see Fig. 1, shows that the ground-state energy is not well described by the Lang-Firsov approximation.

We now consider the effect of including the memory function $M_{i\alpha,j''\alpha''}(z)$ in the Green's function in Eq. (8) with $\gamma=1$. The energy of such a “dressed” polaron E_p compares well with the exact calculation for three sites, see Fig. 1. $E_p + \varepsilon_p$ gives the lowering of the energy of the polaron due to the self-energy corrections involving the exchange of one or more phonons. What physically occurs is that a polaron at site *i*, $|\varepsilon_{p0}(i)\rangle$ with $\varepsilon_{pm} = -\varepsilon_p + m\hbar\omega$, couples via the effective hybridization term to states with an (excited) polaron at neighboring site *j* while leaving behind excited phonon states at site *i*. This gives a state $|\varepsilon_{pm}(j); (n-m)\hbar\omega(i)\rangle$ with energy $\varepsilon_{pm} + (n-m)\hbar\omega = -\varepsilon_p + n\hbar\omega$. This coupling can be clearly seen from $\text{Im}[M_{i\alpha,j''\alpha''}(z)]$, see the inset in Fig. 1. An estimate of the kinetic energy can be obtained by replacing the multiplet of phonon states by its maximum,

which is approximately at $-\varepsilon_p + n_{\max}\hbar\omega \cong -\varepsilon_p + 2g\hbar\omega = \varepsilon_p$. From this two-state problem one easily obtains a kinetic energy of $\varepsilon_p - \sqrt{\varepsilon_p^2 + 2t^2}$. This is significantly larger than the Lang-Firsov result, showing the importance of the inclusion of self-energy effects in the calculation of the ground-state energy.

As shown in Eq. (9), the needed lowering of the on-site polaronic self-energy occurs when the given polaron has two empty neighboring sites as seen from the $\langle 1 - n_{j\bar{a}} \rangle$ term. This effect would disappear if these sites were occupied so this on-site renormalization effectively simulates a near-neighbor repulsion. Note also that the repulsion only occurs along the ferromagnetic bonds. In addition, the size of the polaronic energy is greatest for the $3z^2 - r^2$ orbital with its lobes pointing in the direction of these ferromagnetic bonds strongly suggesting orbital ordering as well as charge ordering. The other self-energy effect leads to incoherent hopping between two different sites and is small [$t_{\text{incoh}} = (te^{-\gamma^2 s})^2$].

In the treatment of the temperature dependence of the core spin we follow the approach of de Gennes.¹³ The core spins are distributed according to a molecular field H_{eff} , giving a partition function

$$Z_{\text{spin}} = \int_0^\pi d\theta \sin \theta \exp(-\lambda \cos \theta) = \frac{2 \sinh \lambda}{\lambda}, \quad (11)$$

where $\lambda = g\mu_B\beta SH_{\text{eff}}$, with $\beta = 1/k_B T$. From Z_{spin} one can derive the on-site magnetization

$$m = \frac{1}{Z_{\text{spin}}} \frac{\partial Z_{\text{spin}}}{\partial \lambda} = -\frac{1}{\lambda} + \coth \lambda \quad (12)$$

and the entropy

$$-TS = -T \frac{\partial}{\partial T} (k_B T \ln Z_{\text{spin}}) = k_B T (\lambda m - \ln Z_{\text{spin}}). \quad (13)$$

Furthermore, we need the expectation values $\langle \cos \theta_{ij} \rangle = m^2 \cos \Theta_{ij}$ and

$$\left\langle \cos \frac{\theta_{ij}}{2} \right\rangle = -2 \sum_{l=0}^{\infty} \frac{P_l(\cos \Theta_{ij})}{(2l-1)(2l+3)} \frac{j_l^2(-i\lambda)}{j_0^2(-i\lambda)}, \quad (14)$$

where Θ_{ij} gives the canting angle if *i* and *j* belong to different sublattices and is zero otherwise, P_l is a Legendre polynomial and j_l a spherical Bessel function. The free energy is then given by

$$F = -\frac{1}{\beta} \sum_{\mathbf{k}\nu} \ln(1 + e^{-\beta(\varepsilon_{\mathbf{k}\nu} - \mu)}) + H_{\text{polaron}} + H_{\text{sup}} - TS, \quad (15)$$

where $\varepsilon_{\mathbf{k}\nu}$ are the effective quasiparticle eigenenergies obtained from the Green's function in Eq. (8) with ν the band index.

The free energy and the on-site magnetization of the two lowest-energy magnetic structures are given in the upper part of Fig. 2. In the calculation we have taken $U=1.2$ eV, $\varepsilon_p=0.3$ eV, $\hbar\omega=50$ meV, and $J=8.4$ meV; the matrix elements $t_{i\alpha,j\alpha'}$ are expressed in terms of $(dd\sigma)=0.37$ eV.¹⁴ The self-energy in the polaronic phase is obtained from exact

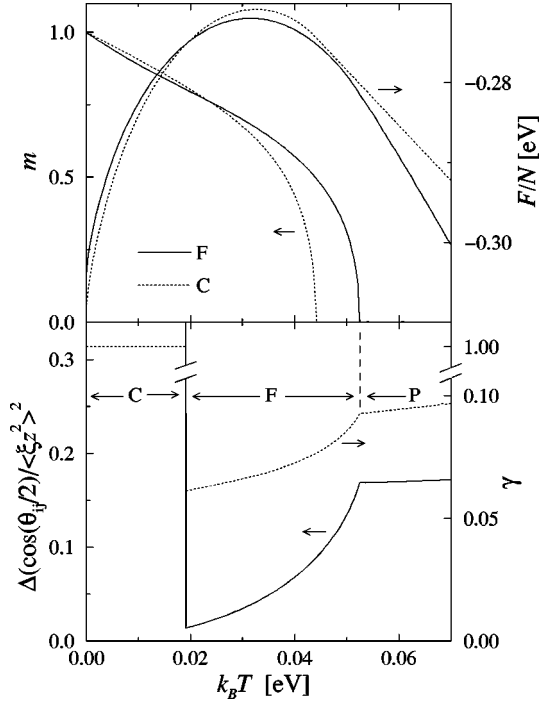


FIG. 2. The upper part shows the on-site magnetization m and the free energy per site F/N for the F (solid) and C (dotted) type magnetic structures. The lower part shows the renormalization of the resistivity $\Delta[\cos(\theta_{ij}/2)]\langle\xi z^2\rangle^{-2}$ (solid line) and the degree of polaron coupling γ (dotted line) for the magnetic structure with the lowest free energy. For decreasing temperature the system goes from paramagnetic (P) to ferromagnetic (F) to C type. When going from F to C the resistivity increases by several orders of magnitude.

diagonalization of the Hamiltonian on small clusters. For this range of parameters, the two magnetic structures with the lowest energy at low temperatures are a basically metallic ferromagnetic state and a C -type polaronic charge-ordered state. When decreasing the temperature we observe that the system first becomes ferromagnetic. At a somewhat lower temperature, we find the critical temperature for finite on-site magnetization of the C -type structure. However, the system does not undergo a transition to this state, since the free energy of the ferromagnetic state is still lower. A crossing of the free energies is observed at yet a lower temperature. The different behavior of the free energy as a function of temperature can be understood from the stronger sensitivity to thermal fluctuations of the $\langle\cos\theta_{ij}\rangle$ term of the superexchange compared to the $\langle\cos(\theta_{ij}/2)\rangle$ term of the double exchange.

The effects on the resistivity are calculated in the same way as Kubo and Ohata.²² The resistivity is proportional to $\rho \sim (m^*)^2 \Delta[\cos(\theta_{ij}/2)] \sim \Delta[\cos(\theta_{ij}/2)] / (\langle\xi z^2\rangle)^2$, where z is the Coulomb renormalization. The dependence of the term on the right-hand side and the degree of the polaronic effect γ as a function of temperature are shown in the lower part of Fig. 2. We have defined $\Delta[\cos(\theta_{ij}/2)] = \langle\cos^2(\theta_{ij}/2)\rangle - \langle\cos(\theta_{ij}/2)\rangle^2$. For the ferromagnetic state the self-energy effects are negligible and, although the effective quasiparticles become somewhat more polaronic on approaching the Curie temperature, the change in resistivity as a function of temperature is mainly due to the double-exchange effect and is similar to that obtained by Kubo and Ohata.²²

When the system undergoes a transition to the C type the resistivity jumps by approximately $\exp(2\varepsilon_p/\hbar\omega)$, i.e., 5 orders of magnitude. The temperature dependence of the resistivity for the C type is more difficult to obtain since, in a system where the coherent bandwidth is so strongly reduced, conduction properties are most likely dominated by impurities.

We can summarize the situation as a function of temperature as follows. At low temperature the superexchange between the t_{2g} spins and the electron phonon coupling stabilize the polaronic state. The strong reduction of the coherent bandwidth by $\exp(-\varepsilon_p/\hbar\omega)$ explains the insulating nature of the polaronic state. However, the kinetic energy of simple polarons is too small to explain the ferromagnetic couplings and the charge order in the observed CE structure. A calculation of the self-energy to order t^2 shows that the polarons have a finite size. For a $3z^2 - r^2$ polaron the energy can be lowered by ferromagnetically aligning the t_{2g} spins in the z direction. The electron can now make virtual hopping processes along the ferromagnetic bond to a neighboring site forming an (excited) polaron and leaving behind excited phonons. Further delocalization does not occur since it would cause a trail of excited phonon states. This on-site self-energy is only present if the neighboring sites are empty as a result of the $\langle 1 - n_{j\alpha}^- \rangle$ term in Eq. (9). This effective repulsive energy leads to a charge-ordered state. The occupancies of the different sublattices are 0.78 and 0.22 electrons per site.

For higher temperatures the ferromagnetic state is stabilized with respect to the polaronic state, since the $\cos(\theta/2)$ term in the double exchange is less sensitive to variations in the angle between the core spins θ than the $\cos\theta$ term in the superexchange. The ferromagnetic state is stabilized by the kinetic energy of the e_g electrons which is maximum when the state is nonpolaronic ($\gamma=0$), which directly implies that also the polaronic self-energy is zero. One therefore finds normal metallic behavior and no charge order (i.e., 0.5 electron per site).

Let us look in somewhat more detail into the different types of polaronic states. The 50-50 charge-ordered Mn lattice can be viewed as being built up of blocks containing a “localized” e_g polaron at the center surrounded by four antiferromagnetic and two ferromagnetic nearest-neighbor t_{2g} core spins. The nearest-neighbor transfer-matrix elements \bar{t} in the self-energy are maximum for an e_g polaron in a $3z^2 - r^2$ orbital with its lobes directed along the ferromagnetic bonds. This situation is shown in Fig. 3. For ferromagnetic bonds in the xy plane, there are two orthogonal orientations of these building blocks denoted by $+1$ (ferromagnetic bonds at 45° with respect to the x axis) and -1 (ferromagnetic bonds at -45° with respect to the x axis). We now place these blocks on this lattice according to the formula $(-1)^{a_x n_x + a_y n_y}$, where n_x and n_y are integer coordinates, along the x and y axes, respectively, of the occupied polaronic state. For different coefficients a_x and a_y one generates the C ($a_x = a_y = 0$), CE ($a_x = 0, a_y = 1$), and E ($a_x = a_y = 1$) type magnetic structures.

The different stabilities of these structures are most likely a result of lattice strain.²³ In general, the ferromagnetic bond is somewhat longer than the antiferromagnetic one, as a result of differences in the Mn-O-Mn bond angle. Taking this into account, we directly see that the E structure is incom-

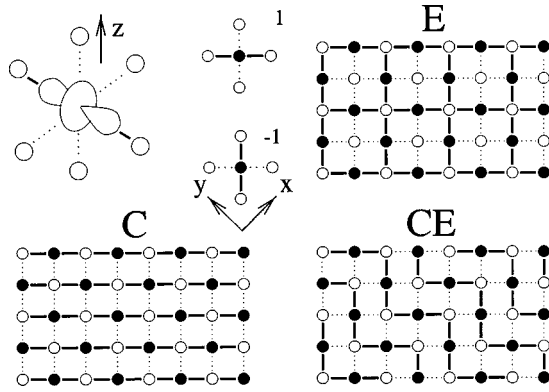


FIG. 3. The polaronic states are built up of blocks containing a localized $3z^2-r^2$ polaron at the center, surrounded by two ferromagnetically (solid lines) and four antiferromagnetically (dotted lines) aligned nearest-neighbor sites. Viewed from the z axis there are two possible ways (indicated by 1 and -1) of placing the ferromagnetic bonds in the xy plane, which are shown schematically in the figure. The charge-ordered lattices show the simplest ways of placing the “dressed” polarons in the xy plane by using the formula $(-1)^{a_x n_x + a_y n_y}$ (see text): C ($a_x = a_y = 0$), CE ($a_x = 0, a_y = 1$), E ($a_x = a_y = 1$).

mensurate, which is probably the reason why it has not been observed experimentally.⁶ Furthermore, the C structure has a larger strain than the CE phase. In addition to that, due to the angular dependence of the transfer-matrix elements, hopping processes in the CE structure can lead to double occupancy of the formally Mn^{4+} sites due to the 90° angles in the ferromagnetic chains, thereby lowering the energy. In the C structure with ferromagnetic chains along the z axis, on the other hand, the transfer matrix elements of the $3z^2-r^2$ with the x^2-y^2 orbitals are zero.

Therefore, for $x = \frac{1}{2}$, the CE structure is the energetically most favorable. As mentioned above, maximum transfer-matrix elements \bar{t} in the self-energy are obtained for polarons in $3z^2-r^2$ orbitals with the lobes along the ferromagnetic chains that zigzag in the xy plane. This is in agreement with the experimentally observed orbital ordering. The C -type structure is found for higher hole-doping values x where, due to the smaller electron densities, the effects of strain and double occupancy become less important.

The charge order in these systems is a result of the $\langle 1 - n_{j\alpha}^- \rangle$ term in Eq. (9). This term suppresses virtual incoherent-hopping processes to occupied neighboring sites. This preference for empty neighboring sites leads to an ef-

fective repulsive interaction. However, polarons only repel each other along ferromagnetic bonds, since the hopping processes in the self-energy do not take place along the antiferromagnetic bonds due to the $\cos(\theta/2)$ term. This explains why the charge order in the xy plane of the CE structure can reproduce itself in the z direction, since consecutive planes are coupled antiferromagnetically. This is in contrast with charge order resulting from a Coulomb repulsion between polarons which would be the same in all directions.

Summarizing, we have shown that the metal-insulator transitions in $A_{1/2}A'_{1/2}MnO_3$ are of a nonpolaronic to polaronic type. If one would consider only the small double-exchange coupling due to the coherent hopping of the polarons, the insulating phase would be purely antiferromagnetic, i.e., G type, due to the superexchange between the core spins. However, we have shown that the polarons are dressed by virtual hopping processes to neighboring sites involving the exchange of one or more phonons. For $x=0.5$, we find that, for polarons in the $3z^2-r^2$ orbital, the self-energy corrections ferromagnetically align the neighboring spins along the z axis. In the xy plane the hybridization matrix elements in the self-energy are smaller and the t_{2g} superexchange aligns the neighboring spins antiferromagnetically. Furthermore, since the self-energy results from hopping processes to neighboring sites, occupancy of these sites suppresses the self-energy. This effectively leads to a repulsive interaction along the ferromagnetic bonds. One thus obtains basic units which, in the case of the perovskites at $x=0.5$, consist of a $3z^2-r^2$ polaron with four antiferromagnetically and two ferromagnetically aligned nearest-neighbor core spins and a preference for empty neighboring sites along the ferromagnetic bonds. Placing these units on a lattice naturally leads to the charge-ordered C , E , and CE structures, of which the CE structure has the lowest energy for $x=0.5$. These basic units are most likely also of importance in explaining structures found for doping levels other than $x=0.5$, such as, e.g., the recently observed stripe phases.²⁴ The anisotropy of the double-exchange coupling of an e_g polaron might also explain the presence of antiferromagnetic fluctuations found in the paramagnetic state,²⁵ which is thought to be of a polaronic nature.²⁶

In agreement with experiment we observe, for a well-chosen set of parameters, a transition from the ferromagnetic to the CE -type structure as a function of temperature. Due to the strong phonon renormalization of the bandwidth, this transition is accompanied by a jump in the resistivity of several orders of magnitude.

*Present address: Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

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